Stereospecific chlorination of polyacetylene by chemical doping*

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We present a novel utilization of chemical doping in stereospecific chlorination to π-conjugated polyene. It has been verified that not only prolonged $FeCl_3$ doping but also iodine doping followed by chlorine addition to one-dimensional conjugated polyene (polyacetylene, $(CH)_x$) produce a stereoregular chlorinated polyacetylene, $(CHCl)_x$, i.e. di-syndiotactic poly(1,2-dichloroethylene). In the latter case, tacticity of the polymer, defined as the ratio of stereoregular to atactic segments in the $(CHCl)_x$, strictly depends upon the dopant concentration of iodine before the chlorine addition. Thus chemical doping is a promising method to control the tacticity of $(CHCl)_x$ without polymerization. We demonstrate that the positively charged polyene segment generated by the chemical doping plays an essential role in governing stereospecific chlorination.

(Keywords: polyacetylene; chemical doping; chlorination; stereospecificity; stereoregularity; tacticity)

INTRODUCTION

Regularity in the spatial arrangement of a polymer chain is called stereoregularity, and it specifies the polymer configuration. In practical usage, stereoregularity has been linked with tacticity since Natta's pioneering work on the stereospecific polymerization of propylene[1]. It is undoubtedly true that the configuration, and therefore the stereoregularity, of polymers is determined during the polymerization reaction, and is never altered, even by a structural change such as an internal rotation around the polymer skeleton. This forms a striking contrast to conformational change. Nevertheless, if the stereoregularity could be modified or controlled under a particular condition, such as a chemically or electronically perturbed environment, it might lead to an advanced stage of reaction design for stereoregular polymers.

Stereochemistry and regiochemistry in chemical reaction, on the other hand, are represented by stereospecificity and regiospecificity or regioselectivity, respectively. Electrophilic addition of halogen or alkyl halide to olefins, including finite conjugated polyenes, has been one of the central subjects in stereospecific and regiospecific chemical reactions and therefore has been extensively investigated[2–5]. For instance, electrophilic additions of chlorine to ethylene, butadiene and hexatriene have been shown to proceed by 1,2-*trans* (*anti*), 1,4-*cis* (*syn*), and 1,6-*trans* (*anti*) attack, respectively. This stereospecificity has been rationalized with a mixing rule of σ–π orbital interaction[6–8]. Although the first-step attack of the halogen molecule is characterized by the 1,2*n* addition and can even be predicted by the mixing rule, there is no guarantee that subsequent additions to the remaining double bonds in the cases of butadiene and hexatriene will proceed with a manner similar to the first step, yielding stereoregular products. Furthermore, it is still an open question whether the above-mentioned 1,2*n* addition also holds in the longer conjugated polyenes. In fact, the reaction between 1,3-butadiene and HBr produces a mixture of 3-bromo-1-butene (71%, 1,2-addition) and 1-bromo-2-butene (29%, 1,4-addition)[9]. Besides, the reaction of π-conjugated polyene (polyacetylene, $(CH)_x$) and chlorine produces an atactic chlorinated polyacetylene. This is caused by the simultaneous occurrence of 1,2*n* additions, which results in a random addition product[10].

Recently we have elucidated that prolonged chemical doping with $FeCl_3$ on $(CH)_x$ gives a stereoregular chlorinated polyacetylene, $(CHCl)_x$, which has been confirmed to be a poly(1,2-dichloroethylene) with di-syndiotactic (dst) structure[10] (*Scheme 1*).

$$(CH)_x \xrightarrow{FeCl_3\text{ doping}} [CH^{y+}(FeCl_4^-)_y]_x \xrightarrow[\text{Stereospecific chlorination}]{\text{Prolonged } FeCl_3\text{ doping}} \text{dst}\,(CHCl)_x$$

Scheme 1

Current evidence indicates that the $FeCl_3$ doping of $(CH)_x$ with an appropriate concentration of dopant gives rise to a remarkable increase in electrical conductivity by virtue of the formation of doped polyacetylene, $[CH^{y+}(FeCl_4^-)_y]_x$. However, subsequent doping for a prolonged time or with excess dopant concentration causes a drastic decrease of conductivity, towards the level of an insulator, owing to chlorination of the conjugated polyene[11]. In spite of this, the chlorinated polyacetylene thus generated is intriguing because of its stereoregularity, which enables its use as a precursor of carbyne, that is one-dimensional polyyne consisting of only *sp* carbon atoms[12].

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Through spectroscopic and theoretical analyses of the chlorination mechanism, it has been clarified that π-electron charge polarization on positively charged polyene segments, produced by chemical doping using an electron-accepting dopant such as $FeCl_3$, is essential to the stereospecificity and regiospecificity underlying the present chlorination[13]. It is therefore anticipated that the use of another kind of dopant species would also afford a foundation for stereospecific addition to conjugated polyenes by means of chemical doping.

In this study, we have focused on the direct chlorination of chemically doped $(CH)_x$ by using both iodine (I_2) as a dopant and chlorine (Cl_2) as an addition reagent under several conditions; we have tried to establish a relationship between dopant concentration before chlorination and the degree of stereoregularity, and hence tacticity of the polymer product.

EXPERIMENTAL

Synthesis of polyacetylene films

Polyacetylene films of the so-called S-type $(CH)_x$ were synthesized according to a well-established method[14]. The Ziegler–Natta catalyst was prepared by dissolving tetra-*n*-butoxytitanium, $Ti(OBu)_4$, and triethylaluminium, $AlEt_3$, in toluene ($[Ti] = 0.5\,mol\,l^{-1}$ and $[Al]/[Ti] = 4$); it was then aged at room temperature for 30 min. Polymerization of acetylene was carried out at $-78°C$ for 10 min. The polyacetylene film thus obtained was washed with toluene and dried under vacuum pumping. The *cis* content of the as-grown film was more than 90% (*cis*-rich film) and the bulk density was $0.3–0.5\,g\,cm^{-3}$.

Mechanically stretchable polyacetylene films were synthesized by the 'non-solvent polymerization method' using a catalyst aged at high temperature[15]. The catalyst solution for acetylene polymerization was prepared by dissolving $Ti(OBu)_4$ and $AlEt_3$ in cumene ($[Ti] = 0.4\,mol\,l^{-1}$ and $[Al]/[Ti] = 4$); it was subsequently aged at 150°C for 3 h. Using the catalyst aged at high temperature, polymerization was carried out at $-78°C$ under the condition where the solvent was evaporated completely through dynamic pumping before introduction of acetylene gas. The polymerization was allowed to continue for about 16 h. After washing with toluene and drying in vacuum, *cis*-rich, high density polyacetylene films suitable for stretching were produced; the *cis* content was more than 90% and bulk density more than $1.0\,g\,cm^{-3}$. These films were mechanically stretched to yield aligned films with draw ratios of 4–5. Orientation of the films was confirmed by the appearance of dichroism with respect to both in-plane and out-of-plane vibrational modes in the polarized i.r. absorption spectra[16,17].

These two kinds of polyacetylene—S-type $(CH)_x$ and mechanically stretchable $(CH)_x$—were used for synthesis of chlorinated polyacetylenes to be used for measurements of i.r. absorption spectra and X-ray diffraction photographs, respectively.

Preparation of chlorinated polyacetylene

Chlorinated polyacetylenes, $(CHCl)_x$, were prepared using four methods for the chlorination of $(CH)_x$ films. The methods may be classified as follows.

Direct chlorine addition
1. Gas phase
2. Liquid phase

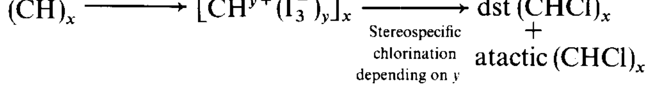
Chlorination via chemical doping
3. Iodine doping followed by chlorine addition in liquid phase
4. Prolonged $FeCl_3$ doping

The degree of chlorine addition to $(CH)_x$ is defined as y in $(CHCl_y)_x$, i.e. a molar ratio of Cl to CH unit. The value of y is evaluated by measuring the weight uptake of the film after chlorination. Similarly, the degree of iodine doping of $(CH)_x$ is also expressed by y in $(CHI_y)_x$ and evaluated from the weight uptake after doping.

1. Gas phase. The polyacetylene film was brought into contact with chlorine gas in a closed system which had been subjected to vacuum before chlorination. In order to achieve a homogeneous chlorination, the pressure of chlorine was controlled at less than 0.133 kPa in the initial stage of chlorination. The chlorine pressure was gradually increased up to 2.67–4.00 kPa; this was accompanied by a change in colour of the film from metallic dark blue to grayish white.

2. Liquid phase. A solution of chlorine in carbon tetrachloride (CCl_4) was prepared by trapping an appropriate volume of chlorine gas with liquid nitrogen (77 K) and then dissolving it in the CCl_4 solvent. The polyacetylene films were immersed in three different CCl_4 solutions with chlorine concentrations of 0.005, 0.05 and $0.2\,mol\,l^{-1}$. In the case of the $0.05\,mol\,l^{-1}$ solution, the film became grayish white then colourless within 0.5–3 h. The degree of chlorine addition, y, was 0.85–0.95. However, no change was observed in the dilute solution of $0.005\,mol\,l^{-1}$ even after 72 h. On the other hand, rapid chlorination was observed in the $2.0\,mol\,l^{-1}$ solution, yielding a film too fragile to be handled for spectroscopic measurements. Therefore, the $0.05\,mol\,l^{-1}$ solution was used for direct chlorination in the liquid phase.

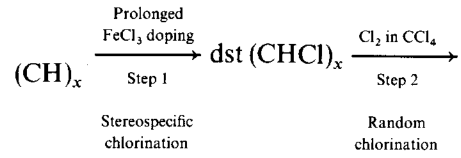
3. Iodine doping followed by chlorine addition in liquid phase. CCl_4 solutions of iodine with concentrations of 0.1 wt%, 0.3 wt% and saturation were prepared in order to control the degree of iodine doping to $y < 0.07$, $y = 0.07–0.15$ and $y > 0.15$, respectively. The films were immersed in these solutions for 0.2–24 h and were then dried in vacuum. The dopant concentration, y in $(CHI_y)_x$ ranged from 0.01 to 0.32. Subsequently the iodine-doped films were immersed in a CCl_4 solution of chlorine. Within 0.2–2 h the films became semi-transparent, indicating the chlorination of the iodine-doped polyacetylene films. After immersing for 6 h, the films were dried in vacuum. These films were a greenish white colour and the degree of chlorine addition was 0.85–0.95 (*Scheme 2*).



$$(CH)_x \xrightarrow{I_2\text{ doping}} [CH^{y+}(I_3^-)_y]_x \xrightarrow[\substack{\text{Stereospecific}\\ \text{chlorination}\\ \text{depending on } y}]{Cl_2\text{ in }CCl_4} \begin{array}{c}\text{dst }(CHCl)_x\\ +\\ \text{atactic }(CHCl)_x\end{array}$$

Scheme 2

4. Prolonged $FeCl_3$ doping. The polyacetylene film was immersed in a saturated solution of $FeCl_3$, using nitromethane as a solvent, for 6–48 h. After washing with nitromethane, the film was dried in vacuum. The chlorinated film, with a chlorination degree of 0.70–0.95, was brown-green or yellow-green in colour (*Scheme 3*).



$$(CH)_x \xrightarrow[\text{Step 1}]{\text{Prolonged FeCl}_3\text{ doping}} \text{dst}\,(CHCl)_x \xrightarrow[\text{Step 2}]{Cl_2\text{ in }CCl_4} \text{dst}\,(CHCl)_x + \text{atactic}\,(CHCl)_x$$

Scheme 3

Measurements

I.r. absorption spectra of both chemically doped and chlorinated polyacetylene films were measured with a *FT*i.r. spectrometer (JASCO FTIR-8000).

Measurements of X-ray diffraction patterns of chlorinated polyacetylenes were carried out using a CuKα-ray (wavelength 1.542 Å) produced by an X-ray generator (JEOL-JDX-8F) equipped with a cylindrical camera. The conditions were: voltage, 35 kV; current, 18 mA; irradiation time, 24 h.

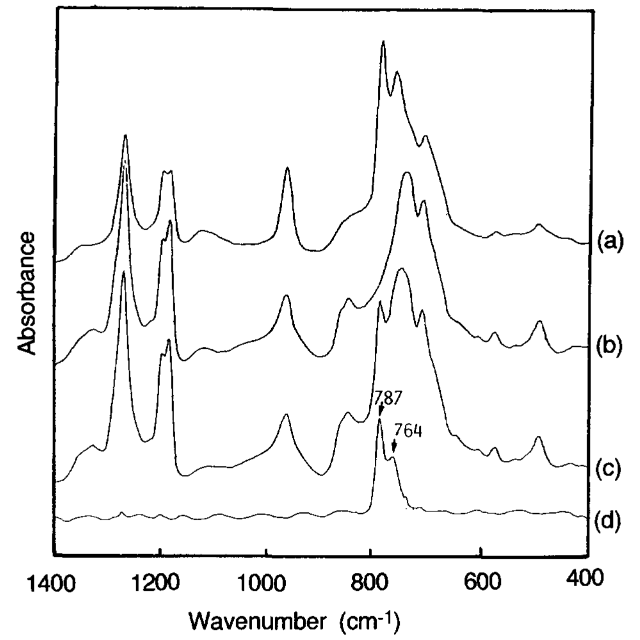


Figure 1 Infra-red absorption spectra of $(CHCl)_x$ prepared by: (a) liquid phase chlorination; (b) gas phase chlorination; (c) gas phase followed by liquid phase chlorination. (d) Difference spectrum of (c) − (b)

RESULTS AND DISCUSSION

Comparison between gas phase and liquid phase direct chlorinations

Figure 1 shows i.r. absorption spectra of chlorinated polyacetylene prepared by direct chlorine additions. It is clear that the chlorine addition is insufficient only with the gase phase chlorination. That is, the gas phase chlorinated polyacetylene is further chlorinated in the liquid phase giving new absorption peaks at 787 and 764 cm^{-1}, both of which are assigned to C–Cl stretching vibrations. Therefore, we will adopt the liquid phase chlorinated polyacetylene as a directly chlorinated film.

Figure 2 shows i.r. spectra of chlorinated polyacetylenes prepared by several different procedures. *Table 1* shows the main assignments of absorption peaks for a typical sample of chlorinated polyacetylene, $(CHCl)_x$.

It may be helpful in understanding the structural difference between several chlorinated polyacetylenes to focus on absorption peaks ranging from 700 to 800 cm^{-1}. This is because these peaks are ascribed to C–Cl stretching vibrations which sensitively reflect chemical structure around chlorine atoms in the chlorinated polyacetylene. In *Figure 2a*, three absorption peaks at 787, 764 and 710 cm^{-1} overlap each other giving a broad band. In *Figure 2b*, absorption intensities at 787 and 764 cm^{-1} decrease, while those at 743 and 710 cm^{-1} increase. In addition, the absorptions at 1193 and 1183 cm^{-1}, both assigned to C–H bending modes and that at 494 cm^{-1} for the C–Cl bending mode, become

Table 1 Main assignments of i.r. absorption peaks of $(CHCl)_x$ composed of stereoregular and atactic structures

Wavenumber (cm^{-1})	Vibrational mode
2981	C–H stretching
1268	C–H bending deformation
1193	C–H bending deformation
1183	C–H bending deformation
976	C–C–C chain deformation
787	C–Cl stretching
764	C–Cl stretching
743	C–Cl stretching
710	C–Cl stretching
494	C–Cl bending deformation

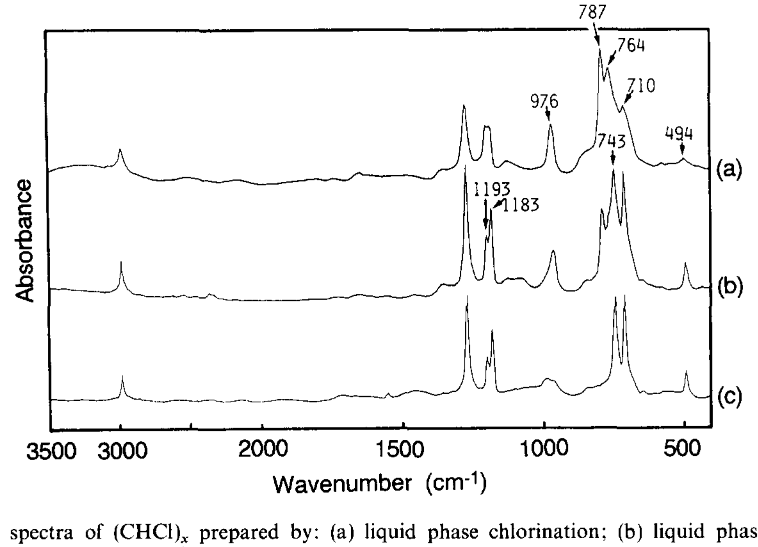


Figure 2 Infra-red absorption spectra of $(CHCl)_x$ prepared by: (a) liquid phase chlorination; (b) liquid phase chlorination of iodine-doped polyacetylene, $(CHI_{0.14})_x$; (c) prolonged $FeCl_3$ doping of undoped $(CH)_x$

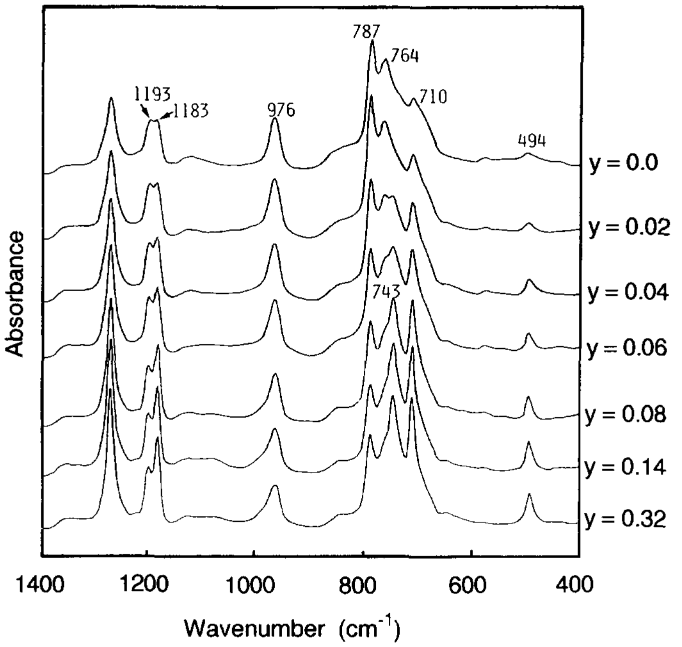


Figure 3 Infra-red absorption spectra of $(CHCl)_x$ prepared by liquid phase chlorination of iodine-doped polyacetylene, $(CHI_y)_x$, with various dopant concentrations, y

sharper and increase in intensity. This tendency can be seen more clearly in *Figure 3*, which shows i.r. absorption spectra of chlorinated polyacetylenes prepared by liquid phase chlorination of iodine-doped $(CH)_x$ with various dopant concentrations. It is clear from this figure that as the dopant concentration increases, the absorption intensities at 743 and 710 cm^{-1} increase, whereas those at 787 and 764 cm^{-1} decrease. At the same time, the absorption intensities at 1193, 1183 and 494 cm^{-1} also increase.

Now let us return to *Figure 2c*, which corresponds to the chlorination through prolonged $FeCl_3$ doping which has been shown[10] to give a stereoregular chlorinated polyacetylene, dst $(CHCl)_x$. The spectrum of *Figure 2c* seems to be intrinsic to *Figure 2b* when the spectrum feature is regarded as a function of the dopant concentration. Namely, only two absorption peaks for C–Cl stretching vibrations remain at 743 and 710 cm^{-1}, whereas the absorption peak for C–C–C chain deformation at 976 cm^{-1} is greatly decreased in intensity.

Comparison between the i.r. spectra of *Figures 2b* and *c* suggests that chlorination of the iodine-doped $(CH)_x$ also produces a stereoregularly chlorinated polymer segment, as in the case of prolonged $FeCl_3$ doping of the neat $(CH)_x$. Thus we may classify absorption peaks of chlorinated polyacetylene into two types, i.e. absorption peaks due to direct chlorine addition (976, 787, 764 cm^{-1}) and those due to chlorination via chemical doping (1193, 1183, 743, 710, 494 cm^{-1}). This means that at least two kinds of chlorinated polymer segments exist with different configurations. As exemplified in *Figure 3*, the ratio between the two types depends on the dopant concentration before chlorination. This will be discussed later in more detail.

X-ray diffraction

Figure 4 shows X-ray diffraction pattern of the uniaxially aligned $(CHCl)_x$ films prepared by various chlorination methods. The photographs in *Figures 4b* and *c* are typical fibre diagrams, indicating a periodic structure of polymer chain. Using both the distance between the zeroth (equatorial) and the first lines in the fibre diagram and Polanyi's equation[18], the fibre period corresponding to the unit cell length was calculated to be 5.2±0.1 Å. On the other hand, the photograph in *Figure 4a* shows a Debye–Scherrer ring, although a faint diffraction resembling a fibre diagram is also seen. (Note that the diffraction points on the equatorial line are due to the polyacetylene fraction that remains even after chlorination.) It follows that there is no distinct fibre period on the directly chlorinated polyacetylene. This indicates that almost all of the chlorinated polyacetylenes prepared by the direct chlorination are atactic polymers having no stereoregular configuration.

From the results of i.r. absorption spectra and X-ray diffraction analyses, we can make the following points. The chlorinated polyacetylene prepared by chemical

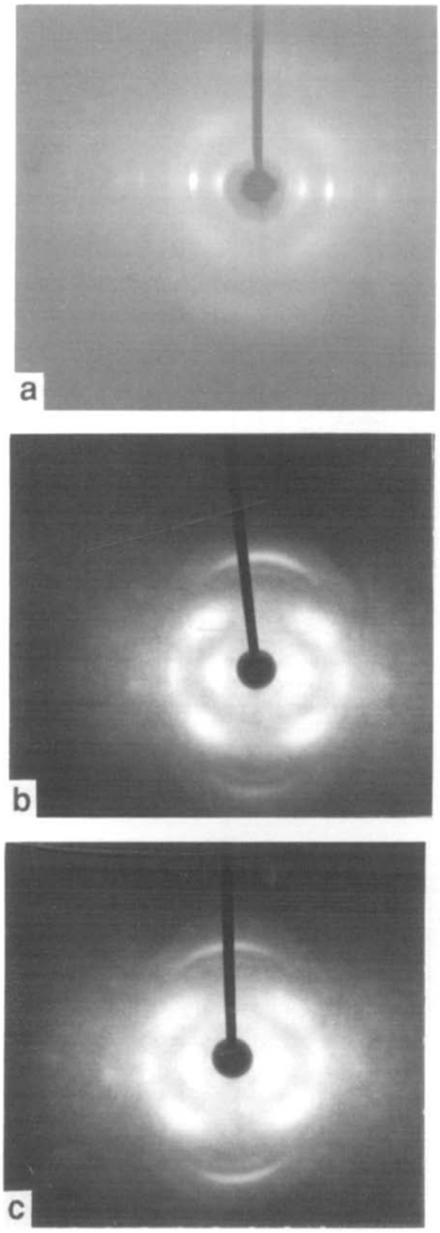


Figure 4 X-ray diffraction patterns of oriented $(CHCl)_x$ prepared by: (a) liquid phase chlorination; (b) liquid phase chlorination of iodine-doped polyacetylene, $(CHI_{0.14})_x$; (c) prolonged $FeCl_3$ doping of undoped $(CH)_x$

doping is a stereoregular polymer with a fibre period of 5.2 ± 0.1 Å; it can be characterized by some i.r. absorption peaks, C–H bending vibrations at 1193 and 1183 cm^{-1}, C–Cl stretching vibration at 743 and 710 cm^{-1}, and C–Cl bending vibration at 494 cm^{-1}. On the other hand, the chlorinated polyacetylene prepared by direct chlorine addition is an atactic polymer. The i.r. absorption peaks of C–C–C skeleton deformation at 976 cm^{-1} and C–Cl stretching vibrations at 787 and 764 cm^{-1} could be indexes to distinguish this type of atactic polymer from the stereoregular one.

Geometrical structure

In order to elucidate the geometrical structure of the chlorinated polyacetylene, *ab initio* crystal orbital calculations were carried out on three kinds of structural models for poly(1,2-dichloroethylene), i.e. erythro-di-isotactic (e-dit), threo-di-isotactic (t-dit), and di-syndiotactic (dst) structures[10] (*Figure 5*). These structures are assumed to be planar zigzag forms with all-*trans* (*trans–trans*, T_2) conformation of the carbon skeleton. The dst structure is confirmed to be the most energetically favourable structure: it is more stable by 33–36 kcal mol^{-1} per $C_2H_2Cl_2$ unit than the e-dit and t-dit structures, leading to the relatively stability: dst > e-dit > t-dit.

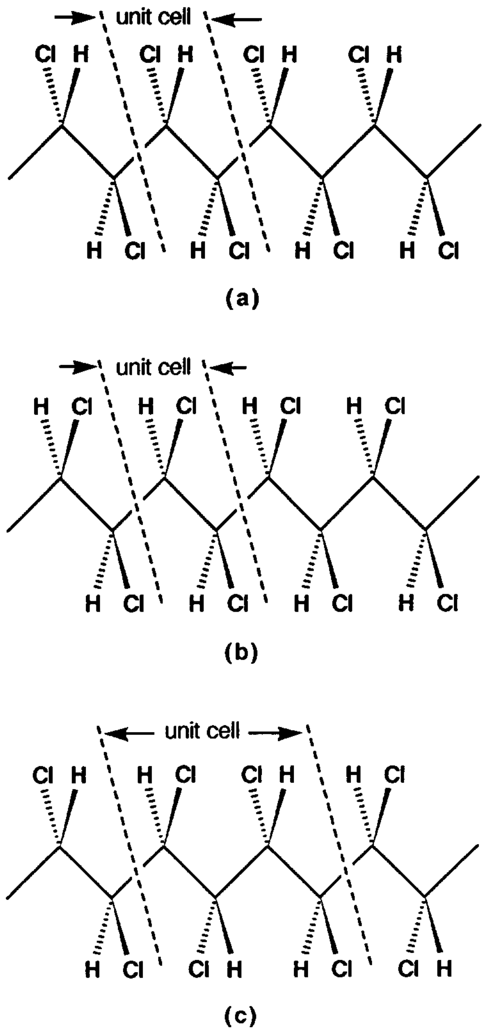


Figure 5 Structural models of $(CHCl)_x$: (a) erythro-di-isotactic (e-dit); (b) threo-di-isotactic (t-dit); (c) di-syndiotactic (dst). These structures are assumed to be planar zigzag forms with all-*trans* (T_2) conformation of carbon skeletons

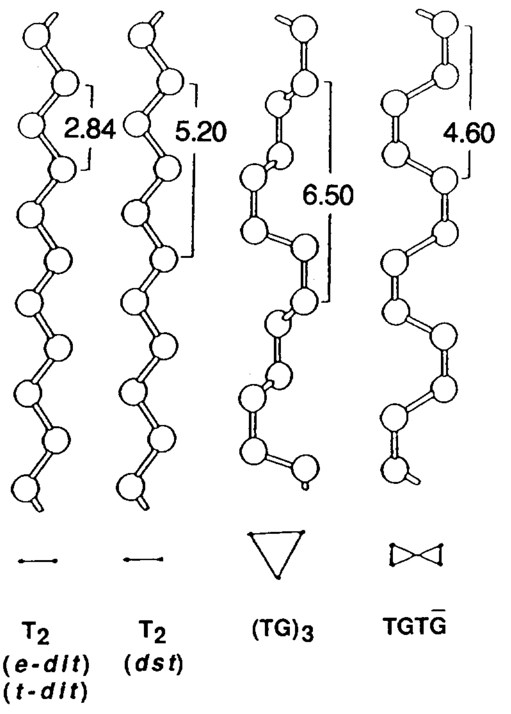


Figure 6 Schematic representation of carbon skeleton chains of structural models and their unit cell lengths corresponding to fibre periods. Measurements are in Ångström

Using optimized geometrical parameters, the unit cell length for the e-dit, t-dit, and dst structures with T_2 conformation were evaluated, as well as those of $(TG)_3$ and $(TGTG)_2$ forms. Note that the $(TG)_3$ and $(TGTG)_2$ forms are non-planar helical structures of *trans–gauche* conformation with three- and two-fold screw axes, respectively. Their unit lengths were determined by employing optimized bond lengths and angles for the dst structure with T_2 form. The results are shown in *Figure 6*.

It is evident that the unit cell length of 5.2 Å on the dst structure is in good agreement with the experimental value of 5.2 ± 0.1 Å determined by X-ray diffraction measurement for the chlorinated polyacetylene prepared by the prolonged $FeCl_3$ doping. As a consequence, we can argue that chlorination through chemical doping gives a stereoregular $(CHCl)_x$, identified as a dst poly(1,2-dichloroethylene).

Factor group analysis

Di-syndiotactic polymer. The dst structure of poly(1,2-dichloroethylene) belongs to a factor group which is isomorphous to a point group of C_{2h}, as shown in *Figure 7*. Based on this symmetry, a factor group analysis for normal vibrations is carried out. The result is summarized in *Table 2*.

The number of normal vibrations within a unit cell, Γ_{vib}, is expressed as follows:

$$\Gamma_{vib} = 9A_g + 8B_g + 8A_u + 7B_u$$

From these vibrations, i.r.-active modes are selected according to a selection rule derived from group theory:

$$\Gamma_{IR} = 8A_u + 7B_u$$

Assuming that internal coordinates of four C–Cl bonds can be expressed as S_1, S_2, S_3 and S_4, and their nuclear displacements as δS_1, δS_2, δS_3 and δS_4, the C–Cl stretching modes are represented by the following

Table 2 Factor group analysis of $(CHCl)_x$ with di-syndiotactic (dst) structure

C_{2h}	E	$C_2(y)$	i	$\sigma_g(xz)$	N	T_r	R_0	n	I.r.	Raman
A_g	1	1	1	1	9	0	(R_y)	9	inactive	active
A_u	1	1	-1	-1	9	T_y	0	8	active	inactive
B_g	1	-1	1	1	9	0	$(R_x), R_z$	8	inactive	active
B_u	1	-1	-1	1	9	T_x, T_z	0	7	active	inactive
U_R	12	0	0	0						
ψ_R	0	π	π	0						
$\pm 1 + 2\cos\psi_R$	3	1	-3	1						
$U_R(\pm 1 \pm 2\cos\psi_R)$	36	0	0	0						

The definitions and meanings of the symbols used are the same as those in standard books treating group theory[24,25]

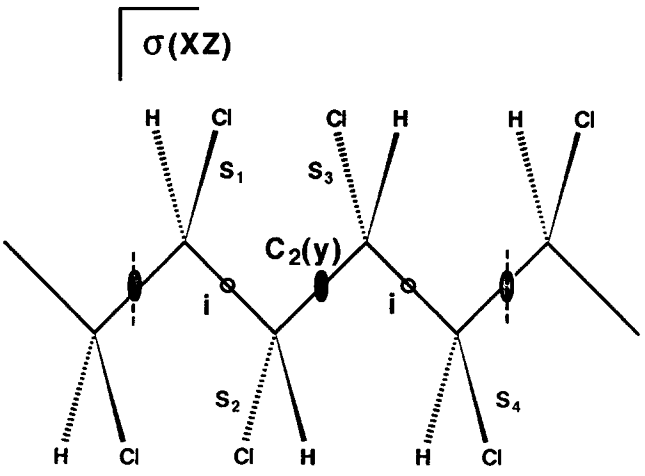
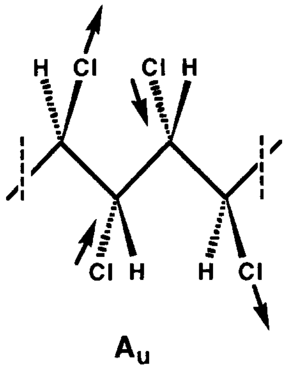


Figure 7 Symmetry elements of di-syndiotactic $(CHCl)_x$

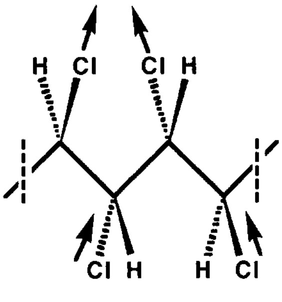
formulae:

$$A_u = \delta S_1 - \delta S_2 - \delta S_3 + \delta S_4$$

$$B_u = \delta S_1 - \delta S_2 + \delta S_3 - \delta S_4$$



A_u



B_u

These C–Cl stretching vibrational modes should be responsible for the two kinds of absorption peak observed at 743 and 710 cm^{-1} in the i.r. spectrum measured in the stereoregular $(CHCl)_x$ (e.g. see *Figures 2b* and *c*).

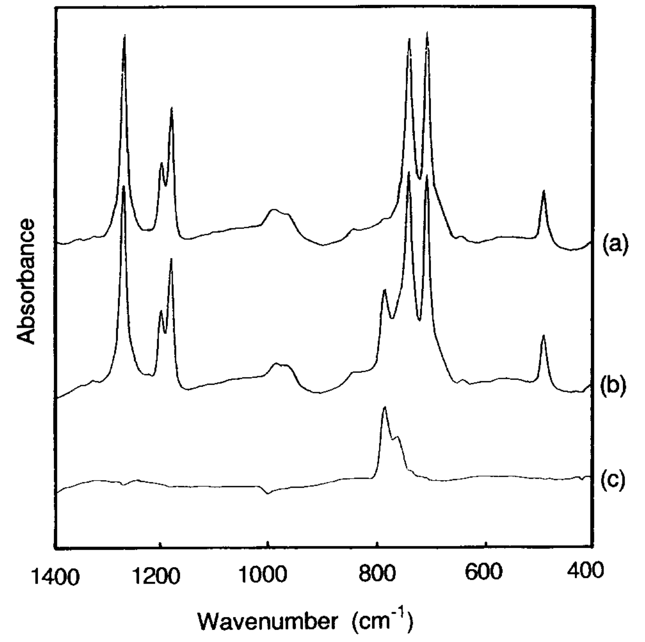


Figure 8 Comparison of i.r. spectra of $(CHCl)_x$ prepared by (a) prolonged $FeCl_3$ doping and (b) prolonged $FeCl_3$ doping followed by liquid phase direct chlorination using Cl_2. (c) Difference spectrum of (b)−(a)

Atactic polymer. Since there is neither strereoregularity nor tacticity in atactic $(CHCl)_x$, it is impossible to perform a factor group analysis for this sort of polymer. However, we can suppose that for the atactic polymer: (i) even i.r.-active modes, in terms of the local site of polymer segment, might be depressed owing to mutual cancellation of dipole moments arising from several polymer configurations; and/or (ii) inherently i.r.-inactive modes might become active due to a lack of symmetry points. The weakening of the absorption peak ascribed to the C–Cl bending mode at 494 cm^{-1} and the strengthening of the C–C–C skeleton mode at 976 cm^{-1} in the atactic polymer may be correlated to cases (i) and (ii), respectively (see *Figures 1* and *2*). It should be noted that the presence of sharp absorption peaks at 787 and 764 cm^{-1} (*Figures 1* and *3*) may imply a partial formation of stereoregular segments even in the apparently atactic $(CHCl)_x$. However, these peaks are located at higher wavenumbers than the two peaks at 743 and 710 cm^{-1} characteristic to the dst structure of $(CHCl)_x$. This may indicate that the former peaks reflect more activated stretching motions and/or stronger C–Cl bonds associated with larger force constants of this bond. This point must await more detailed studies.

Relation between stereoregularity and dopant concentration

It is evident from the present results that $(CHCl)_x$ can be classified into two types of structure: a stereoregular dst structure and an atactic structure. The ratio in which they exist depends on the dopant concentration of the doped polyacetylene before chlorination. This suggests that tacticity of the $(CHCl)_x$ might be controlled by the degree of chemical doping of $(CH)_x$ before chlorination (see *Scheme 2*). We tried to evaluate quantitatively the ratio of dst to atactic structures by means of i.r. absorption spectroscopy.

As shown in *Figure 8a*, prolonged $FeCl_3$ doping of the $(CH)_x$ film produces a chlorinated $(CHCl)_x$ which has i.r. absorption peaks ascribed to the dst structure. In addition, as shown in *Figures 8b* and *c*, immersion of the $(CHCl)_x$ film into CCl_4 solution of chlorine (0.05 mol l^{-1}) results in a random chlorination on unchlorinated polyene segments remaining in the $(CHCl)_x$ film, giving i.r. absorption peaks attributed to atactic structure.

Here we assume that the prolonged $FeCl_3$ doping (step 1 in *Scheme 3*) yields only dst $(CHCl)_x$ and the subsequent direct chlorine addition (step 2) yields only atactic $(CHCl)_x$. Secondly, we suppose that a Lambert–Beer rule holds for each step of the $(CHCl)_x$ structure.

$$A_{dst} = \varepsilon_{dst} c_{dst} d = \varepsilon_{dst} w_{dst} \quad (1)$$

$$A_{at} = \varepsilon_{at} c_{at} d = \varepsilon_{at} w_{at} \quad (2)$$

where A_{dst} and A_{at} represent absorption intensities for vibrations of dst and atactic polymer segments, respectively. In practice, absorption intensities of C–Cl stretching vibrations located at 710 cm^{-1} (dst) and 787 cm^{-1} (atactic) are adopted as A_{dst} and A_{at}, respectively. Similarly, ε_{dst} and ε_{at} are absorption coefficients for these vibrations. c_{dst} and w_{dst} are, respectively, the concentration (g cm^{-3}) and the weight per unit area (g cm^{-2}) of the dst segment; c_{at} and w_{at} are the corresponding values for the atactic segment. d is the thickness of the $(CHCl)_x$ film consisting of dst and atactic segments. These vibrations are chosen for the analysis because they are well separated in the spectrum, while the remaining two peaks at 743 cm^{-1} (dst) and 764 cm^{-1} (atactic) overlap in their tail regions, which makes it difficult to extract inherent intensities of these absorptions.

From equations (1) and (2), one obtains the following relation:

$$A_{at}/A_{dst} = (\varepsilon_{at}/\varepsilon_{dst})(w_{at}/w_{dst}) \quad (3)$$

Hence the fraction of the dst segment in $(CHCl)_x$ is calculated by:

$$\begin{aligned} T_{dst} &= w_{dst}/(w_{at} + w_{dst}) \\ &= (\varepsilon_{at}/\varepsilon_{dst})[(\varepsilon_{at}/\varepsilon_{dst}) + (A_{at}/A_{dst})]^{-1} \quad (4) \end{aligned}$$

Now let us evaluate the values of A_{at}/A_{dst} and T_{dst} in equations (3) and (4). The value of W_{dst} is obtained from a weight uptake from $(CH)_x$ to $(CHCl)_x$ through chlorination by prolonged $FeCl_3$ doping (step 1 in *Scheme 3*), and similarly that of w_{at} through direct chlorination (step 2 in *Scheme 3*). Several sets of the weight ratio w_{at}/w_{dst} and the absorbance ratio A_{at}/A_{dst} are accumulated by varying the concentration of the $FeCl_3$ dopant in step 1, which should affect the degree of chlorination reaction in $(CHCl)_x$. Meanwhile, the concentration of chlorine in CCl_4 solvent (step 2) is kept constant (0.05 mol l^{-1}). The results are shown in *Figure 9*. It is clear that the absorbance ratio is proportional to the ratio of weight uptake. The proportional coefficient — the gradient of the straight line in *Figure 9* — gives a ratio of absorption coefficient between dst and atactic segments in the chlorinated polyacetylene, i.e. $\varepsilon_{at}/\varepsilon_{dst} = 3.7$. Using this value, equation (4) is rewritten as follows:

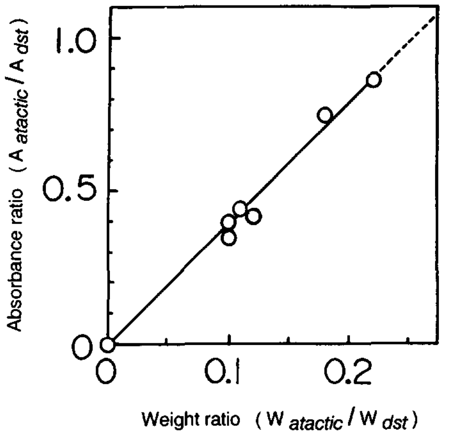


Figure 9 Relationship between absorbance ratio and weight uptake ratio

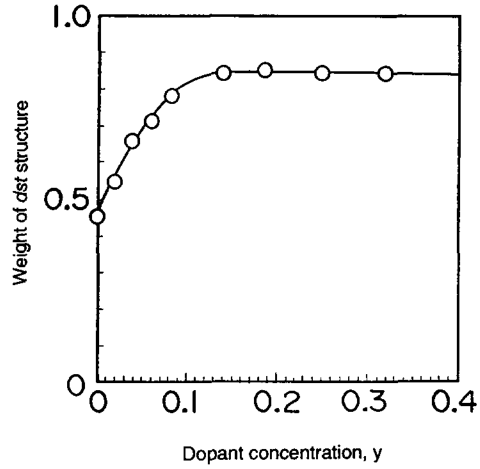


Figure 10 Dependency of $(CHCl)_x$ tacticity upon dopant concentration of iodine, y, as defined in $(CHI_y)_x$

$$T_{dst} = (3.7)[3.7 + (A_{at}/A_{dst})]^{-1} \quad (5)$$

The analytical formula of equation (5) is practically applied to the chlorination described in *Scheme 2*, in order to confirm a relationship between the iodine-doping concentration ($y = 0.02$–0.32) and tacticity of chlorinated polyacetylene. Based on i.r. absorption data shown in *Figure 3*, the fraction of the dst structure of this system is evaluated. The result is described in *Figure 10*.

As the dopant concentration, y, increases, the dst fraction increases and becomes saturated, i.e. $T_{dst} = 0.47$ for $y = 0$ and $T_{dst} = 0.84$ for $y = 0.14$. It is worth noting that even when the dopant concentration is zero, the dst fraction is not zero but a finite value such as 0.47. This means that the stereoregularly chlorinated polyacetylene can be partly produced even by direct chlorination in the liquid phase using CCl_4 solvent. This may be due to chemical doping of chlorine occurring in an initial stage of the reaction between Cl_2 and polyacetylene, as has been verified by previous work[10,11]. In this case, however, the chlorine-doped polyene segments are not as stable as iodine-doped segments, so chlorine addition occurs instantly, mainly in a random manner and partly in a stereospecific fashion, especially around the doped region.

In connection with this result, it is worthwhile to remark that the dopant concentration of $y = 0.14$ is very close to the value marking the point at which some physical properties are drastically changed. For instance, electron spin resonance measurement[19] shows that unpaired electron density of polyacetylene decreases remarkably at the dopant concentration of 0.15. Photomodulated spectroscopy measurement shows that at the same dopant concentration an absorption band appears, indicating a transition from soliton lattice to metallic lattice[20]. Murthy *et al.*[21] have pointed out from X-ray diffraction analysis that a homogeneous stacking structure is formed, composed of both partially doped polyene layer and undoped polyene layer at a doping concentration of 0.13. Assuming that the form of the dopant species is I_3^-, the dopant concentration of 0.14, for instance, means that there is a dopant anion and hence a counter-cation located on the polyene for every ~20 carbon atoms in the polymer chain. This is expressed by a molecular equation such as:

$$[(CH)^{+0.14}(I^-)_{0.14}]_x \approx [(CH)^{+0.14}(I_3^-)_{0.046}]_x$$

CONCLUSIONS

The present study has shed light on an unexplored aspect of chemical doping of conjugated polyenes. We have verified that direct chlorine addition to an iodine-doped $(CH)_x$ gives a stereoregular $(CHCl)_x$, as in the case of prolonged $FeCl_3$ doping of a neat $(CH)_x$. Common to both cases are the positively charged polyene segments generated by the chemical doping, in which the alternative charge polarization is spread along the polymer chain[13,22,23].

Using a new semi-empirical equation, we have evaluated polymer tacticity as a fraction of the stereoregular dst segment in $(CHCl)_x$. In the chlorination through iodine doping, the tacticity of $(CHCl)_x$ is determined by the degree of doping before chlorine addition. This means that the stereospecific chlorination depends on how much the positively charged polyene segments are generated by the chemical doping that is responsible for electron transfers from neutral polyene segments of $(CH)_x$ to electron-accepting dopants. From another point of view, it also means that undoped polyene segments still remaining in partially doped $(CH)_x$ would suffer a random chlorination due to simultaneous occurrence of 1,2*n* additions, yielding atactic segments in the chlorinated polyacetylene.

We have demonstrated that the chemical doping described here enables the control of stereospecificity of chlorination reactions to polyenes. It is expected that an ultimate understanding of the potential utility of chemical doping should disclose a way to establish both stereochemistry and regiochemistry for polymer reactions.

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